

# THE EFFECT OF INORGANIC SPECIES ON CHAR FORMATION FROM BIOMASS FUELS

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## INTRODUCTION

Inorganic species naturally present in biomass play a dual role in terms of the thermochemical properties of biomass and its char. They dramatically affect the temperature and extent of pyrolysis, and many are effective catalysts for combustion and gasification reactions of the resulting char. Previous work in this laboratory (1) on the effect of prepyrolysis treatment of wood with gasification catalysts has indicated that inorganic species naturally present in wood are exchangeable with ions added from solution. Glucuronic acid groups which are present in the hemicellulose fraction of wood, particularly in the acetyl 4-O-methylglucuronoxylans which comprise the hemicellulose fraction of hardwoods, are the most likely sites for ion exchange. Free phenolic groups in the lignin fraction are another probable exchange site. This study was undertaken to determine the role of exchangeable cations on char formation and to further examine the nature of ion exchange in wood. Thus, samples of untreated and acid-washed wood were treated with solutions of the two most prevalent naturally-occurring inorganic species in wood, calcium and potassium; and the effect of the treatments on the thermal decomposition of the wood was determined by thermogravimetry (TG) and derivative thermogravimetry (DTG). The results indicate the mode of addition of gasification catalysts added to wood and their effects on carbonization.

## EXPERIMENTAL

The primary sample used in this study was a well-characterized sample of black cottonwood, *Populus trichocarpa*, a common North American hardwood. Douglas fir, *Pseudotsuga menziesii*, was used as a secondary sample to confirm specific trends in a softwood species. Samples were ground and sieved and the 20-40 mesh fraction was retained. The chemical composition of both samples is given in Table I.

TABLE I  
ANALYSIS OF WOOD SAMPLES AND THEIR ASH CONTENT

Species	Percent		Na	Inorganic Analysis ( $\mu\text{g/g}$ wood)				
	Ash	Lignin		K	Mg	Ca	Mn	Fe
Cottonwood	0.41	20.3	18	668	324	869	<5	5
Douglas fir	0.10	27.4	3	32	53	314	20	<3

Wood samples were treated with potassium carbonate or calcium acetate for TG analysis by soaking in a 0.013 N solution of the salt for 30 minutes and removing excess solution by filtration with suction. For preparation of ion-exchanged samples, the filtered wood was then stirred for 30 minutes in distilled, degassed water to remove adsorbed salts and dried at 40°C under reduced pressure. In some cases, the distilled water wash was eliminated to provide samples treated at a level beyond the exchange capacity of the wood with adsorbed salts.

Acid-washed wood and cellulose samples were prepared by placing 10 g of the sample in 200 ml of 0.1 N HCl and stirring for 4 hours at room temperature. The suspension was then filtered and the wood was washed with 2 liters of distilled water, covered with distilled water and stirred overnight. The sample was filtered again,

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placed in a cellulose extraction thimble and washed for 4 hours in a Soxhlet extractor. The sample was then dried at 70°C under reduced pressure.

Thermogravimetry was carried out using a Perkin-Elmer TGS-2 system which was interfaced to a microcomputer for data acquisition and temperature program control. For determination of char yields, one milligram of sample was heated in a platinum pan to the desired temperature at 25°C/min under flowing nitrogen. This system was also used for ash determinations, in which case the sample was heated to 550°C at 20°C/min under a mixture of O<sub>2</sub> and N<sub>2</sub> and held at 550°C for 10 min. Ash determinations made in this way agreed with those determined on a large scale by standard methods to within 0.02%.

Surface areas of chars were determined gravimetrically using a Cahn R-100 electrobalance (sensitivity = 0.1 µg) equipped with a Cahn adsorption tube. Isotherms were determined for 5-10 mg samples by monitoring carbon dioxide adsorption at room temperature. Surface areas were calculated by application of the Dubinin-Polanyi equation (2).

## RESULTS AND DISCUSSION

The effects of acid washing and addition of calcium and potassium salts on the ash content, char yield and decomposition temperature of cottonwood, Douglas fir and cellulose samples are shown in Table II. The ash contents of the ion-exchanged

TABLE II  
EFFECTS OF VARIOUS TREATMENTS ON MINERAL CONTENT, CHAR YIELD (HTT 600°C)  
AND TEMPERATURE OF MAXIMUM WEIGHT LOSS IN WOOD AND CELLULOSE

Sample and Treatment	Ash Content (%, d.a.f.)	Char Yield (%, d.a.f.)	Temperature of DTG Peak (°C)
COTTONWOOD			
Untreated	0.40 ± 0.03	12.8 ± 0.1	387 ± 2
Acid washed, 0.1% HCl	<0.01	9.8 ± 0.4	379 ± 1
Acid washed, potassium added from solution	0.40 ± 0.05	17.2 ± 0.4	366 ± 1
Acid washed, calcium added from solution	0.27 ± 0.04	12.7 ± 0.3	394 ± 1
Acid washed, calcium and potas- sium added from solution	0.36 ± 0.01	12.4 ± 0.3	393 ± 3
Potassium added from solution	0.45 ± 0.05	14.1 ± 0.5	375 ± 1
Calcium added from solution	0.34 ± 0.03	11.5 ± 0.3	389 ± 1
Hot water, 6 hr. @ 60°C	0.26 ± 0.01	11.2 ± 0.3	391 ± 1
DOUGLAS FIR			
Untreated	0.10 ± 0.01	15.7 ± 0.3	385 ± 1
Acid washed, 0.1% HCl	<0.01	13.4 ± 0.3	388 ± 1
CELLULOSE (CF-11)			
As received	<0.01	5.4 ± 0.3	367 ± 1
Acid washed, 0.1% HCl	<0.01	3.6 ± 0.1	354 ± 2
Acid washed, potassium added from solution (no H <sub>2</sub> O wash)	0.09 ± 0.04	10.6 ± 0.1	392 ± 1
Acid washed, calcium added from solution (no H <sub>2</sub> O wash)	0.13 ± 0.01	5.7 ± 0.1	365 ± 1

cottonwood samples are similar to that of the untreated sample, suggesting that the factors controlling the ash content in wood are related to some extent to ion-exchange capacity. As expected, the calcium-exchanged samples contain less ash in every case because the wood has lower exchange capacity for the divalent calcium cation.

Comparison of the char yields and decomposition temperatures of untreated, acid-washed and ion-exchanged cottonwood samples provides some insight into the overall effect of inorganic species on char formation, as well as contribution of specific cations to the overall effect. It is apparent from the data given in Table II that both the natural ash components and the ions added from solution significantly increase the char yield above that obtained for the ash-free sample. The difference in char yields from untreated and acid-washed Douglas fir samples is less, apparently because of the lower ash content of that sample. As shown in Figure 1, acid washing also has a profound effect on the physical properties of the char. Char from untreated wood retains the original cellular structure of the wood, whereas the original structural features of the wood are lost during carbonization of acid-washed wood. Chars were formed from several substrates under a variety of conditions in order to determine the requirements for loss or retention of physical structure. In general, we found that the physical structure was lost only in acid-washed wood samples and particularly when heated at high rates ( $>500^{\circ}\text{C}/\text{min}$ ). Acid-washed cellulose retained its cellular structure even when heated at very high rates, however.

Because of the possible implications of loss of cellular structure in terms of available surface areas, we measured surface areas of chars prepared at high heating rates from untreated and acid-washed samples of Douglas fir and cellulose. All of the samples had total surface areas of between 800 and 1000  $\text{m}^2/\text{g}$ , indicating the total available surface area is not significantly reduced due to loss of cellular structure in the wood. As seen in Figure 1, it is very likely that the loss of cellular structure in the acid-washed wood is counteracted by foaming of the intermediate char during carbonization.

The most pronounced effect of added inorganics is due to addition of potassium ions, which resulted in an 80% increase in char yield, even at the low concentration afforded by ion exchange. The char yield from the calcium-exchanged cottonwood is more like that of the untreated sample, which suggests that calcium content strongly influences the char yield in this sample. The effect of ion-exchange treatments on the decomposition temperature adds further support to this hypothesis. Potassium treatment reduces the temperature of decomposition, while calcium treatment increases the decomposition temperature. Therefore, the higher temperature of decomposition of untreated wood compared to acid-washed wood can be attributed to the dominant effect of calcium on the decomposition. Addition of potassium and calcium from the same solution (0.007 N in each) gives results very similar to those found for the calcium treatment, which indicates that the calcium is bound preferentially.

The characteristic effects of calcium and potassium on the thermal decomposition of cottonwood provide a means of determining the extent of exchange of ions from solution with naturally-occurring inorganic species. As shown in Table II, addition of potassium and calcium to previously untreated cottonwood results in the same changes in the thermal decomposition patterns as observed for treatment of acid-washed cottonwood, although the effects are less pronounced. Addition of potassium increases the char yield and reduces the decomposition temperature, while addition of calcium reduces the char yield and increases the decomposition temperature slightly. These results indicate that the original ash components can be replaced to some degree by elements added from solution through ion exchange.

Table II also shows the TG results for a cottonwood sample extracted with hot water. This treatment was included primarily to determine whether the hot water Soxhlet extraction step after acid washing might have resulted in swelling of the wood, which could be expected to affect the extent of charring of the wood. As shown in

Table II, the char yield was reduced somewhat by this treatment, but not to the degree observed with acid washing. Furthermore, the hot water extraction increased the decomposition temperature while acid washing decreased the decomposition temperature. In fact, the decomposition pattern is very much like that of calcium-treated cottonwood; thus the reduction in char yield does not appear to be due to physical changes, but rather results from removal of elements such as potassium which tend to reduce the decomposition temperature and enhance charring, allowing the opposing effect of calcium to be more pronounced. The tendency of calcium to be removed less readily from wood by hot water treatment, combined with its preferential addition to wood from solutions containing both potassium and calcium, indicate stronger binding by wood of calcium ions and presumably other alkaline earth metals such as magnesium, which is also present in substantial quantities in many species of wood.

The effects of acid washing and ion exchange treatments on wood decomposition are further illustrated by the DTG's shown in Figures 2 and 3. Figure 2 shows the effect of acid washing on the rate of thermal decomposition of cottonwood and Douglas fir. In both samples, acid washing results in a lower rate of decomposition at low temperatures (250-350°C) and enhances the primary decomposition which peaks near 385°C. Since the low temperature 'shoulder' in the DTG of wood is generally attributed to decomposition of hemicelluloses (3,4), it is apparently the decomposition of this fraction which is most affected by the acid washing. The likelihood of association of inorganic species with the hemicellulose fraction through the glucuronic acid groups further suggests that inorganic species act primarily on the hemicellulose fraction and reduce its decomposition temperature. In the absence of exchanged cations, the hemicelluloses decompose at higher temperatures and produce less char.

Figure 2 shows the effects of several treatments on the DTG of acid-washed cottonwood. The DTG of untreated cottonwood is shown by dotted lines for comparison. The DTG of the potassium-exchanged sample [Figure 2(A)] shows that the low temperature 'shoulder', which was reduced by acid washing is restored by the potassium treatment. The 'cellulose peak' has the same general shape, but is shifted to much lower temperature. With addition of calcium to acid-washed cottonwood [Figure 2(B)], the low temperature shoulder is restored to a lesser extent. When the wood is treated with a solution containing potassium and calcium [Figure 2(C)], the decomposition is identical to that of the calcium-treated wood, except the low temperature shoulder is restored to a greater extent. The DTG of cottonwood which was extracted with hot water, shown in Figure 2(D), is also very much like that of calcium-treated cottonwood. These results indicate that potassium has the greatest effect on the decomposition of the hemicellulose fraction, even though calcium is preferentially bound by ion exchange. However, the overall decomposition of untreated cottonwood, as indicated by the char yield and temperature of the cellulose decomposition is more closely related to the effect of calcium, as discussed previously.

The effects of acid washing and addition of potassium and calcium salts to pure cellulose are also shown in Table II. In this case, the water extraction after the exchange treatment was eliminated, since pure cellulose has few exchange sites and all of the salt was removed by water extraction. These data show that the effects of adsorption of potassium or calcium salts on cellulose decomposition are very different from the effects of the corresponding salts added to wood through ion exchange. Potassium treatment dramatically increases the decomposition temperature of acid-washed cellulose, while it decreases that of wood. The char yield increased in both wood and cellulose. Conversely, treatment of acid-washed cellulose with calcium increases the decomposition temperature only slightly, whereas it dramatically increased the decomposition temperature of wood. Some of these differences may be due to counterion effects, which would be absent in the ion-exchanged wood samples, although these effects are expected to be minimal with the acetate and carbonate salts used in this study. The increase in cellulose decomposition temperature after treatment with potassium has also been noted with other alkali metal salts, particularly sodium (5,6).

The effects of addition of salts to wood beyond the exchange capacity are shown in Figures 4 and 5. These samples were prepared by reducing or eliminating the water wash after ion exchange treatment. Figure 4 shows that the effect of both salts on char yield continues to increase as the level of addition is increased. Thus, adsorbed salts and exchanged cations appear to have similar effects on the char yield in wood, as would be predicted on the basis of the results for adsorption of salts on cellulose.

The dependence of the temperature of the maximum rate of weight loss on level of addition of salts is shown in Figure 5. Surprisingly, adsorption of potassium salts beyond the exchange capacity continues to reduce the decomposition temperature, whereas potassium dramatically increased the decomposition temperature of cellulose. The most likely explanation for this behavior is that the increased potassium treatment continues to decrease the decomposition temperature of the hemicelluloses, and the decomposition products of the hemicellulose fraction catalyze decomposition of the cellulose fraction. Adsorption of calcium on wood reduces the initially high decomposition temperature slightly, which is predictable on the basis of the effects of calcium on cellulose decomposition.

#### CONCLUSIONS

The results of this study show that inorganic species, whether present as components of the natural ash fraction or as added catalysts, have a significant effect on temperature and extent of pyrolysis of wood and even the physical structure of the resulting char. The effects of specific cations added to wood by ion exchange are different from the effects of the corresponding salts adsorbed on cellulose. The overall decomposition of untreated cottonwood appears to be affected primarily by the presence of calcium, which is the predominant component of the ash. However, the decomposition of the hemicellulose fraction, which precedes the primary decomposition of the wood, depends in large part on the presence of potassium ions. The loss of cellular structure in acid-washed wood is believed to be due to enhanced volatilization of the fibrous carbohydrate components which provide the structure of the cell wall. The char then arises primarily from lignin, an amorphous polymer which can flow at high temperatures. Because of the close association of inorganic species with the hemicelluloses through ion exchange, it is very likely that decomposition of the hemicelluloses contributes significantly to char formation in wood.

#### ACKNOWLEDGEMENT

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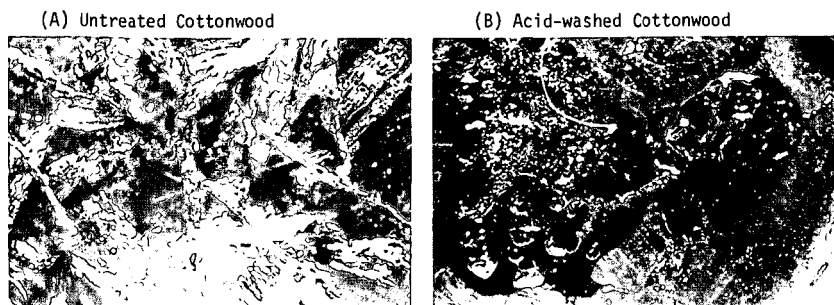


Figure 1. Photomicrographs of chars prepared from untreated and acid-washed cottonwood. (Magnification: 60X)

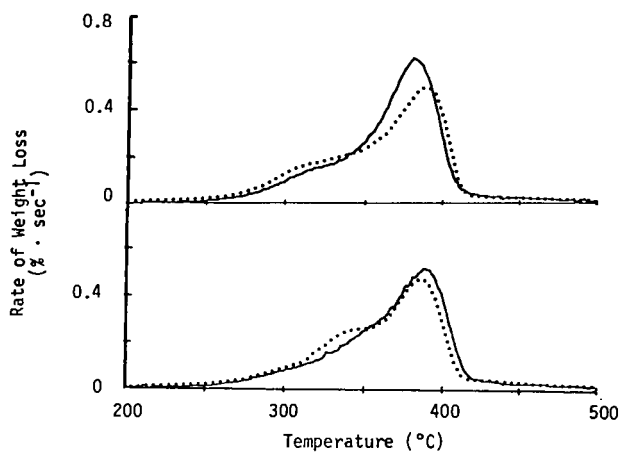


Figure 2. Effects of acid washing on the rate of weight loss (DTG) from cottonwood and Douglas fir. The DTG of the untreated sample is indicated by dotted lines.

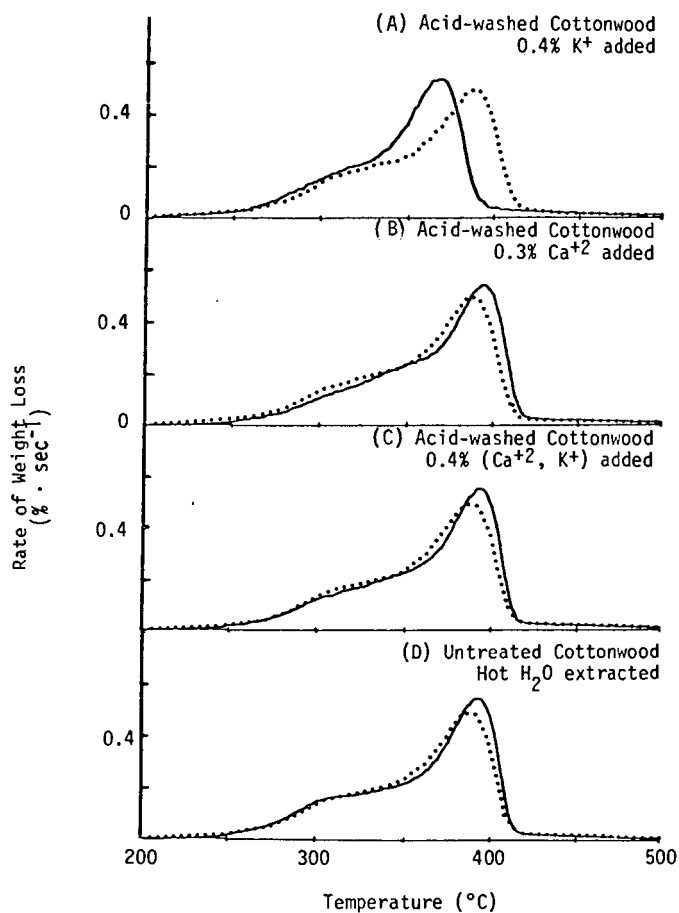


Figure 3. Effects of ion exchange and hot water extraction on the rate of weight loss (DTG) of cottonwood. The DTG of untreated cottonwood is indicated by dotted lines.

Figure 4. Effect of level of addition of calcium (O) and potassium (●) on the char yield from cottonwood.

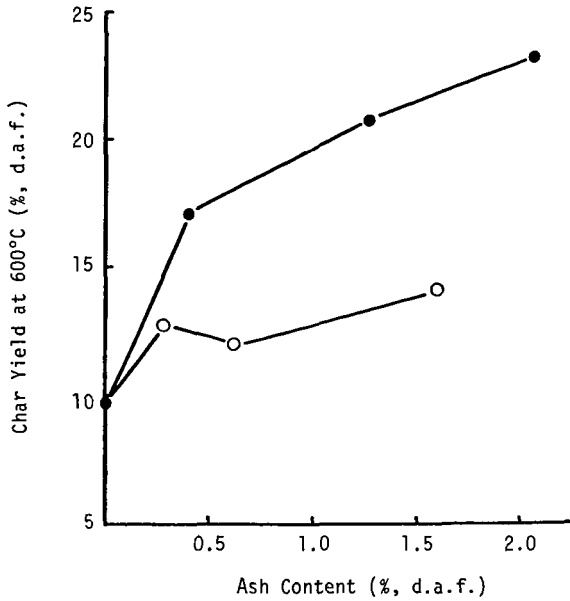


Figure 5. Effect of level of addition of calcium (O) and potassium (●) on the temperature of the maximum rate of weight loss from cottonwood.

